REACTION OF AZOMETHINES WITH ACETOACETIC ESTER

I. SYNTHESIS OF DERIVATIVES OF 1-METHYL-3-PHENYLBENZO[*f*]-QUINOLINE-2-CARBOXYLIC ACID

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The reaction of (benzylidene)(2-naphthyl)amine with acetoacetic ester leads to ethyl 1-methyl-3-phenylbenzo[*f*]quinoline-2-carboxylate. Some reactions of this compound have been studied.

The reaction of (benzylidene)(2-naphthyl)amine (I) with acetoacetic ester (II) has been studied and it has been shown that the presence of a catalyst affects the course of the reaction. When the components were heated in the absence of a catalyst, the noncyclic amino keto ester (III) – ethyl α-acetyl-β-(2-naphthylamino)-β-phenylpropionate – was isolated, its structure being confirmed by spectral characteristics and the results of elementary analysis. The UV spectrum contains three bands due to the absorption of the condensed benzene rings (Fig. 1).

The performance of the reaction in the presence of catalytic amounts of concentrated HCl led to the cyclic product (IV) – ethyl 1-methyl-3-phenylbenzo[*f*]quinoline-2-carboxylate. The structure of (IV) was confirmed by IR and UV spectra and the results of elementary analysis. The IR spectrum lacks the absorption bands characteristic for the stretching vibrations of an NH group and a ketonic C=O. The UV spectrum is typical for compounds of the benzo[*f*]quinoline series [1] (Fig. 1).

We also obtained the ester (IV) from the amino oxo ester (III) by boiling an ethanolic solution in the presence of concentrated HCl. This confirms the hypothesis put forward previously [2], according to which the formation of derivatives of benzo[*f*]quinoline in the reaction of azomethines with compounds containing mobile hydrogen atoms takes place through an amino ketone stage. It is interesting to observe that in the cyclization of (III), in addition to (IV), (benzyl)(2-naphthyl)amine (V) was isolated. Thus, it has been shown experimentally for the first time that in the cyclization of amino ketones to benzo[*f*]quinoline derivatives the acceptor of the protons split out is the azomethine.

On being heated with ethanolic caustic potash, the ester (IV) is readily converted into the water-soluble potassium 1-methyl-3-phenylbenzo[*f*]quinoline-2-carboxylate (VI). It was impossible to isolate the 1-methyl-3-phenylbenzo[*f*]quinoline-2-carboxylic acid in the free state: when an aqueous solution of (VI) was acidified with mineral or organic acids, 1-methyl-3-phenylbenzo[*f*]quinoline (VII), which is the product of the decarboxylation of this acid, was isolated.

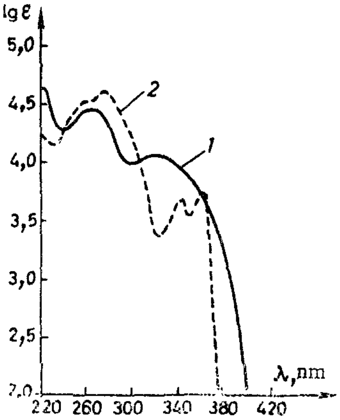

Fig. 1. UV spectra in ethanol: 1) ethyl α-acetyl-β-(2-naphthylamino)-β-phenylpropionate; 2) ethyl 1-methyl-3-phenylbenzo[*f*]quinoline-2-carboxylate.

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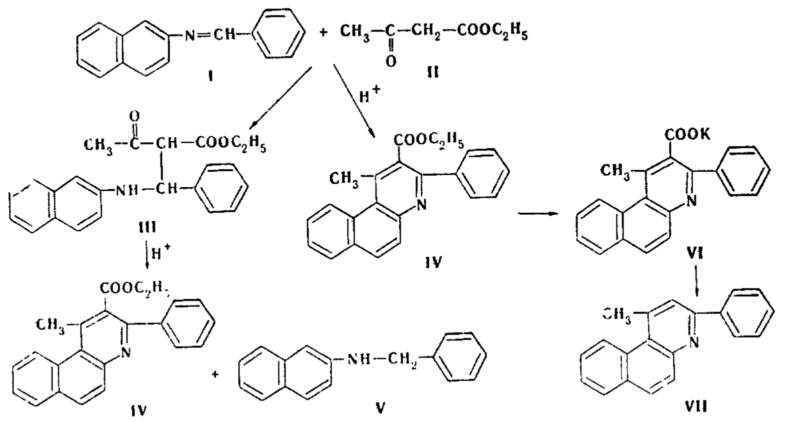

EXPERIMENTAL

The IR spectra were taken on an UR-20 spectrophotometer in tablets with KBr. The UV spectra were taken on an SF-4A instrument in ethanol. The purities and individualities of the compounds obtained were determined by means of the TLC method.

Ethyl α-Acetyl-β-(2-naphthylamino)-β-phenylpropionate (III). A mixture of 2.3 g (0.01 mole) of (benzylidene)(2-naphthyl)amine (I) and 5.2 g (0.04 mole) of acetoacetic ester (II) in 30 ml of ethanol was heated in the boiling water bath for 1 h and cooled, and 2.3 g (64%) of (III) was filtered off. mp 90-92°C (from propan-2-ol). Found, %: C 76.6; H 6.4; N 4.1. $C_{23}H_{23}NO_3$. Calculated,%: C 76.5; H 6.4; N 3.9. IR spectrum, cm^{-1}: 3390 (NH group), 1715 (ketonic C=O), 1740 (ester C=O), 1160-1200 region (C−O−R_{aliph}).

Ethyl 1-Methyl-3-phenylbenzo[*f*]quinoline-2-carboxylate (IV). A mixture of 2.3 g (0.01 mole) of (I), 5.2 g (0.04 mole) of (II), 20 ml of n-propanol, and eight drops of concentrated HCl was heated in the boiling water bath for 1 h, cooled, and neutralized with aqueous ammonium hydroxide to give 1.12 g (33%) of (IV). mp 132-133°C (from a mixture of toluene and propan-2-ol). Found, %: C 81.0; H 5.7; N 4.2. $C_{23}H_{19}NO_2$. Calculated, %: C 80.9; H 5.6; N 4.1.

Cyclization of (III). An ethanolic solution of 3.61 g (0.01 mole) of (III) containing seven drops of concentrated HCl was heated on the boiling water bath for 30 min. Then it was cooled, and the resinous precipitate was filtered off and was boiled with aqueous ammonium hydroxide solution, after which it was triturated with water. This gave 0.11 g (5%) of (benzyl)(2-naphthyl)amine, mp 66-67°C (from propan-2-ol); picrate, mp 140-140.5°C. According to the literature [3], mp 68°C; picrate, mp 140-141°C. The mother solution was neutralized with aqueous ammonium hydroxide and evaporated slightly, and the resin that precipitated was treated with ether, giving 0.56 g (15%) of (IV), mp 132-133°C (from a mixture of toluene and propan-2-ol).

Potassium 1-Methyl-3-phenylbenzo[*f*]quinoline-2-carboxylate (VI). A mixture of 3.41 g (0.01 mole) of (IV) and 70 ml of 40% ethanolic caustic potash was boiled for 2-3 min. The salt (VI) was isolated by evaporating the reaction solution at room temperature, separated from the excess of caustic potash by boiling with propan-2-ol, and recrystallized twice from propan-2-ol. This gave 2.8 g (85%) of (VI), mp 270-272°C. Found, %: K 10.8; N 3.9. $C_{21}H_{14}KNO_2$. Calculated, %: K 11.1; N 3.9. IR spectrum, cm^{-1}: 1380 and 1580 (broad intense bands characteristic for carboxylic acid salts).

1-Methyl-3-phenylbenzo[*f*]quinoline (VII). Dilute hydrochloric acid was added dropwise to a solution of 3.5 g (0.01 mole) of (VI) in 35 ml of H_2O to give a pH of 5. The precipitate of (VII) that deposited was filtered off. The yield of (VII) was 2.1 g (80%), mp 155-156°C (from a mixture of toluene and ethanol). According to the literature [4], mp 155-157°C.

LITERATURE CITED

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